

Process for the synthesis of monocrystalline mass materials comprising nitrides of group III elements by a method using a nitrogen containing solvent and additive

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Abstract of **FR2796657**

The method involves a two stage process under pressure in which the nitride is first obtained in a polycrystalline form and a solvothermal crystallogenesiis is then carried out. A process for the synthesis of monocrystalline nitride crystal masses of group III elements consists in preparing the polycrystalline nitride of at least one of these elements, in finely divided form, then effecting a solvothermal crystallogenesiis. An Independent claim is also included for the nitride monocrystals obtained and microcrystallites.

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<p>(22) Filing date: July 20th, 1999</p> <p>(30) Priority:</p> <p>(43) Date application made publicly available: January 26th, 2001 Bulletin 01/04.</p> <p>(56) List of documents cited in the preliminary search report: <i>Please refer to the end of this specification.</i></p> <p>(60) References to other related national documents:</p>	<p>(71) Applicant(s): <i>THOMSON CSF Corporation. – FR.</i></p> <p>(72) Inventor(s): GERARD DEMAZEAU, BERNARD BERDEU, CECILE COLLADO, ALAIN LARGETEAU, JEAN CHARLES GARCIA, JEAN LOUIS GUYAUX, and JEAN MASSIES.</p> <p>(73) Holder(s):</p> <p>(74) Agent(s): THOMSON CSF.</p>
<p>(54) METHOD FOR SYNTHESIZING BULK SINGLE CRYSTAL MATERIALS COMPRISING NITRIDES OF GROUP III ELEMENTS</p> <p>(57) In order to manufacture bulk single crystals from nitrides such as GaN, we first prepare finely-divided polycrystalline nitride in a pressure chamber, in the presence of a solvent such as NH₃ and an additive such as NH₂NH₃Cl; we then proceed with solvothermal crystallogensis in a chamber (2) containing a mother substance (6), which is the polycrystalline nitride, and seeds (7).</p> <p>[Figure]</p>	

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METHOD FOR SYNTHESIZING BULK SINGLE CRYSTAL MATERIALS COMPRISING NITRIDES OF GROUP III ELEMENTS

The present invention relates to a method for synthesizing bulk single crystal materials comprising nitrides of Group III elements.

Materials associating Group III and V elements have received considerable attention in recent years, especially nitrides of aluminum (AlN), gallium (GaN), and indium (InN). Due to the large forbidden energy gap separating the valence band and the conduction band, these nitrides may, in the pure or doped state (n or p), lead to major industrial developments. Among these we may cite, in non-limiting fashion, high-temperature semiconductors, light-emitting diodes (LEDs), high-density optical storage, etc.

Among these III-V nitrides, GaN is especially interesting due to the intermediary value of its forbidden energy band. In particular, it may lead to the manufacture of light-emitting diodes operating in the blue or ultraviolet spectral region.

The main problem is obtaining single crystals of GaN. Two principal approaches have been explored: one based on thin-layer deposits, and the other aimed at obtaining bulk single crystals.

The first approach is discussed in the following publications: Nakamura, S., Harada, Y., and Seno, M., (1991): "Novel Metal-organic Chemical Vapor Deposition System for GaN Growth," Appl. Phys. Lett., 58 (18), 2021-2023; Nakamura, S., Senoh, M., Iwasa, N., and Nagama, S., (1995): "High-brightness InGaN Blue, Green, and Yellow Light-emitting Diodes with Quantum Well Structures," Jp. J. Appl. Phys. Vol. 34, Part 2, 7A, L797-L799; Nakamura, S., (1997): "First III-V-Nitride-based Violet Laser Diodes," J. Cryst. Growth, 170, 1-15. And in the following patents: "Manufacture of Gallium Nitride Compound Semiconductor Lasers," JP 94-62229, March 31st, 1994; "Manufacture of Nitride Semiconductor Laser Diodes," JP 96-53429, March 11th, 1996.

As regards the second approach (obtaining bulk single crystals), two methods have been tested.

The first method is derived from the melting bath crystallization technique, but given the high temperatures required [$T_{\text{melting}}(\text{GaN}) \approx 3064^{\circ}\text{C}$], very high nitrogen pressures (approximately 2 GPa) were used in order to stabilize the GaN stoichiometry (1.4 - 1.5 GPa). Such pressures appear difficult to implement on an industrial scale due to the energy stored during compression of gases such as nitrogen [publications: Porowski, S., (1996): "High-pressure Growth of GaN – New Prospects for Blue Laser," J. Cryst. Growth, 166, 583-589; Porowski, S., Bockowski, M., Lucznik, B., Wroblewski, M., Krukowski S.T., Grzegory, I., Leszczynski, M., Nowak, G., Pakula, K., and Baranowski, J., (1997): "GaN Crystals Grown in the Increased-volume High-pressure Reactors," Mat. Res. Soc. Symp. Proc., 449, 35-40. Patent: "Method of Manufacturing Epitaxial Layers of GaN or Ga (Al,In)N on Single Crystal GaN and Mixed Ga(Al,In)N Substrates," WO 96-PL 17, October 11th, 1996].

The second method, recently explored by the same authors under the generic term AMMONO [Publication: Dwilinski, R., Doradzinski, R., Garczynski, J., Sierzputowski, L., Baranowski, J.M., and Kaminska, M., (1997), "Exciton Photo-luminescence of GaN Bulk Crystals Grown by the AMMONO Method," Mat. Sci. Eng., B50 46-49], consists of using NH_3 ammonia under supercritical conditions ($T < 500^{\circ}\text{C}$ – $P < 500$ Mpa) starting from the initial metal. The resultant product relates more to a powder than to processing nitride single crystals as the latter are understood by the expert.

The AMMONO method does not make it possible to obtain industrially-usable single crystals: its authors do not describe a reliable crystallogensis stage (no indication is given as to the conditions to be met or the principal parameters of this stage). The articles cited above reveal that the growth of crystallites is random and that their size cannot be controlled.

The goal of the present invention is a method for synthesizing bulk material comprising nitrides of Group III elements that yields industrially-usable and economical single crystals whose size falls within the 2-50 mm range, although this size is in no way limiting.

The method of the invention is characterized by the fact that it consists of preparing a nitride of at least one of said elements in divided form, then in performing solvothermal crystallogeneses.

The present invention will be more fully understood upon reading the detailed description of an embodiment method, cited by way of non-limiting example and illustrated by the attached drawing, the sole figure of which is a simplified cross-section view of a reaction chamber that could be used for implementing the crystallogeneses stage of the method of the invention.

The invention is described below with reference to the synthesis of GaN single crystals, but it is understood that it is not limited to the synthesis of this substance alone, and that it may be implemented for the synthesis of nitrides of Group III elements and their alloys, such as GaInN and GaAlIn, for example. Therefore, each time gallium is involved, it could be replaced by one of these elements or by an alloy of these elements, while taking their specific characteristics into account (specifically, whether they are solid or liquid).

According to the invention, the method for synthesizing such nitrides includes two stages: the first consists of obtaining a gallium nitride in finely-divided form, which will be referred to hereinafter as the "mother substance," and the second consists of carrying out crystallogeneses starting from the mother substance. It should be noted that the size of the mother substance grains plays an important role in the crystallogeneses process, which is described in detail below. This process is closely linked to the transport of a chemical component that potentially contains gallium and nitrogen towards crystallization seeds. To ensure the formation of such a chemical component, it is necessary to give the GaN acting as the mother substance excellent reactivity with the solvent used during this process. The smaller the mother substance grains are (size is preferably smaller than 1 μm), the larger the total surface of a same quantity of mother substance is, and the better the reactivity.

However, given the fact that the method of the invention applies to the synthesis of other nitrides (such as AlN, InN, or nitrides of other Group III elements), the first stage of this method can unfold in different ways; the

condition to meet is to obtain a finely-divided mother substance. Hence, whereas in the case of GaN the encapsulation of the additive by gallium results from gallium's low melting temperature value, in the case of other compounds such as AlN and InN, since the Al⁰ and In⁰ metals are solids (at ambient temperature), the method for preparing the mother substance, although different from that of GaN, is very similar to it. Instead of encapsulation, it involves a homogeneous mixture of metal grains (Al, In, etc.), available in powder form, with additives.

In the case of gallium, the first stage is prepared as follows. The gallium is mixed, at a temperature slightly higher than the temperature at which it becomes liquid, with one or several finely-divided materials, in order to obtain an easy-to-handle powder, and the gallium then encapsulates this/these material(s), which we will refer to as additives. Such an additive may be any finely-divided chemical compound that is likely, upon decomposition, to have a nitriding power or to increase the solvent's nitriding power.

We also found that the additive can play a number of roles: it helps to ensure good division of the metal gallium, which is practically liquid under ambient conditions (its melting temperature is approximately 29.78°C); it enables formation of a divided solid phase, which is more easily handled than a liquid phase, and it takes part, directly or indirectly, in the gallium nitriding phenomenon (this nitriding could be carried out by the nitriding solvent alone, or along with a nitriding additive, or by the solvent and the additive at the same time). If the additive is selected from among nitriding additives such as NaN₃ or NH₂NH₃Cl, the nitriding kinetics in the presence of NH₃ in the supercritical state is much higher than when the solvent NH₃ is used alone. This nitriding kinetics can be improved if the additive or coadditive used also produces, upon decomposition, a hydrogenated atmosphere. This product may be NaBH₄. Generally speaking, additives are advantageously selected from among those that are likely to divide gallium and to encourage its nitriding.

Moreover, the choice of additive is guided by the possibility of easily separating the subproducts of the GaN reaction. Hence, for example, if NaN₃ is used as an additive, the elimination of subproducts containing sodium is difficult,

even harmful for the GaN microcrystallites, due to the alteration of their surface. Advantageously, the method of the invention uses $\text{NH}_2\text{NH}_3\text{Cl}$ or $\text{NH}_3\text{NH}_3\text{Cl}_2$ hydrazinium chlorides as additives. In addition to the very high reactivity of these hydrazinium chlorides in the nitriding process, we have found that the subproduct formed thereby (NH_4Cl) can be easily separated from GaN, either by introducing a temperature gradient between the reaction mixture (mother substance) and the upper end of the chamber containing it (as described below), or by sublimation, by treating the final reaction mixture in a nitrogen flow between 300 and 600°. This treatment lasts between 3 and 10 hours depending upon the mass of treated product.

In the case of synthesis of alloys such as GaInN , AlGaInN , GaAlInN , etc., the gallium may be subdivided by a mixture of powders (Al^0 and/or In^0 and $\text{NH}_2\text{NH}_3\text{Cl}$, for example). The invention also applies to the synthesis of single crystals of nitride alloys implementing at least one of the Group III elements.

In order to successfully complete this stage, in the case of gallium, we optimize the quantities of gallium and additive. One may, for example, select a ratio ranging from 1 to 10 as the $\text{NH}_2\text{NH}_3\text{Cl}/\text{Ga}$ molar ratio. The reaction is performed in a chamber into which the solvent and the reagents (gallium, additive, and possibly Al^0 and/or In^0 and a coadditive) are placed. The solvent may, for example, be NH_3 or NH_2NH_2 , or any other solvent that is compatible with the stability of III-V nitrides.

The reaction mixture is brought to a temperature higher than the critical temperature of the solvent alone ($400 < T < 800^\circ\text{C}$). Since the reaction mixture is contained within a constant volume (chamber volume), the temperature elevation induces a fluid pressure increase. Generally, the pressure ranges from 40 to 400 MPa. Since $T > T_c$ (critical temperature of the solvent alone) and $P > P_c$ (critical pressure of the solvent alone), the fluid is in supercritical conditions. Under these conditions, the formation of GaN microcrystallites is observed. Since the solubility of the reagents introduced into the solvent is very different in subcritical conditions than it is in supercritical conditions, under supercritical conditions we induce bulk nucleation of the GaN, leading to the formation of microcrystallites.

The reaction duration depends upon the reactivity of the additives or coadditives, as well as the values of the temperature and pressure thermodynamic parameters. The resultant microcrystallites of GaN (or one of its alloys) may have dimensions of approximately 1 μm . Along with using them in the second stage described below, they may be used in other applications: manufacture of ceramics, source or target material for laser ablation deposition, gallium chemistry, hardening coatings, material for replacing blue screen phosphors, etc.

Once the GaN microcrystallites are obtained, we proceed with the second stage: the crystallogensis of bulk single crystal GaN. This stage occurs inside a closed reaction chamber, and is referred to as the "solvothetmal" stage. On the drawing, we have shown a sketch of an installation 1 including a reaction chamber 2 shaped like an elongated, vertically-arranged cylindrical receptacle. The chamber 2 is closed at its upper section by a nozzle 3 connected to a pressure control device (not shown). The chamber 2 is arranged in a furnace 4 that surrounds it over its entire height and enables temperature gradients to be applied to it along its axis.

The chamber 2 is divided into two superimposed zones: a lower zone 2A and an upper zone 2B, separated by a diaphragm 5. As a variation, the diaphragm 5 can be eliminated. The temperature gradient existing between these two zones (2A and 2B) is between 10 and 100°C. The gradient direction depends on the solubility of the mother substance as a function of the temperature.

The mother substance 6 developed in the first stage is placed in zone 2A, and several crystallization seeds 7 are suspended in zone 2B. The seeds are composed of segments of single crystal or polycrystalline material that either have lattice parameters that are compatible with those of the GaN network (single crystal), or are oriented so as to ensure heteroepitaxy (that is, coincidence of the crystallographic positions of certain atoms). These seeds may be made of GaN, InN, AlN, or any material having a crystalline structure that is very similar to that of GaN. The chamber 2 is filled with a nitrogenous solvent (for example, hydrazine N_2H_4 or ammonia NH_3) or any solvent that is compatible with

III-V nitrides. The chamber 2 is kept at a pressure ranging approximately from 5 MPa to 2 GPa.

In order to ensure the transport of gallium and nitrogen from the mother substance 6 towards the seeds 7, it is advantageous to form intermediary compounds likely to provide anions, such as N^{3-} or any other combination containing nitrogen, in zone 2A. These compounds result from a chemical reaction between the mother substance GaN and at least one other "precursor" compound. Such a compound improves the solubility of GaN (which is very low, even when it is in the form of very fine grains) and, thanks to the formation of ionic components, encourages the transport of gallium and nitrogen. The intermediary compounds are generally either $Ga(NH_3)_x^{3+}$ complexes or nitrides that are soluble in the solvent filling the chamber. In any case, it is necessary to maintain a temperature gradient between zone 2A, where the intermediary compounds are formed, and the seeds, so that these complex intermediary compounds are broken down into GaN and N^{3-} (or NH_3) and the nitride is redeposited onto the seeds. Given the particular physico-chemical properties of the solvents brought to the supercritical state (temperature and pressure), it is preferable to avoid the formation domain of the complex component $Ga(NH_3)_x^{3+}$ (whose stability is relatively limited) by controlling temperature and pressure conditions in the chamber 2.

Advantageously, formation of a component M_xGaN_y (soluble in a nitriding solvent) that acts as an intermediary between the mother substance GaN and an additive MN_z can lead to the formation of an ionic chemical component that may, depending upon the temperature gradient, transport the gallium and nitrogen towards the seeds when the abovementioned crystallogenes conditions are met. In order to ensure good solubility of the intermediary compound M_xGaN_y , which is indispensable for the formation of the ionic component $GaN^{(1+\delta)3}_{2+\delta}$ which is responsible for the chemical transport of the components of GaN (namely Ga^{3+} and N^{3-}), the substance M may be selected from among any element that increases the ionicity of the Ga-N bond. Advantageously, M may be an alkali element, specifically lithium, and the precursor is then Li_3N .

The parameters influencing the transfer of chemical substances from the mother substance towards the seed are: the nature of the intermediary compound M_xGaN_y , the nature of the solvent, the nature of the seeds, the temperature gradient T between the mother substance and the seeds, the temperature of the mother substance, and the pressure value in the chamber 2. Experiments have demonstrated that by using intermediary compounds for which: M is an alkali or alkali-earth element, the solvent is liquid NH_3 , the temperature of the mother substance ranges from 100 to 600°C, the pressure ranges from 5 MPa to 2 GPa, and the T ranges from 10 to 100°C, one can synthesize GaN single crystals whose dimension may range from 2 to 50 mm, although this size is non-limiting.

The duration of the crystallogenesis process depends upon the quantity of material treated, the chemical parameters able to control transport in such a way [ungrammatical construction; word or words missing] (nature of the solvent, nature and quantity of the additive or coadditive, temperature gradient), the thermodynamic parameters of temperature and pressure, as well as the size of the desired single crystals. Depending upon the latter parameter in particular; durations of 1 to 10 weeks may be necessary.

CLAIMS

1. Method for synthesizing bulk single crystals comprising nitrides of Group III elements, consisting of preparing finely-divided polycrystalline nitride from at least one of these elements, then in performing solvothermal crystallogenesiis.
2. Method according to Claim 1, wherein the divided polycrystalline nitride is prepared using a nitriding additive.
3. Method according to Claim 3, wherein the additive is $\text{NH}_2\text{NH}_3\text{Cl}$ or $\text{NH}_3\text{NH}_3\text{Cl}_2$.
4. Method according to one of the preceding claims, wherein the preparation of polycrystalline nitride is performed in the presence of a nitriding solvent.
5. Method according to Claim 4, wherein the solvent is NH_3 or NH_2NH_2 .
6. Method according to Claim 4 or 5, wherein the nitriding kinetics is increased by using an additive that produces a hydrogenated atmosphere upon its decomposition.
7. Method according to Claim 6, wherein the additive is NaBH_4 .
8. Method according to Claim 6, wherein several coadditives able to play various roles are used conjointly to prepare the polycrystalline nitride.
9. Method according to one of the preceding claims, wherein the preparation of the divided polycrystalline nitride is performed in a chamber under a pressure ranging approximately from 40 to 400 MPa.
10. Method according to one of the preceding claims, wherein crystallogenesiis is performed in a reactive chamber (2) divided into two zones and containing the polycrystalline nitride in one of the zones (2A) and crystallization seeds in the other zone (2B), with a temperature gradient being maintained between the two zones, the chamber being filled with a solvent that is chemically compatible with III-V nitrides and able to transport chemical components containing

gallium and nitrogen, and the seeds being composed of single crystal or polycrystalline material.

11. Method according to Claim 10, wherein the pressure in the chamber ranges approximately from 5 MPa to 2 GPa and wherein the temperature difference between the two zones ranges approximately from 10 to 100°C.
12. Method according to one of Claims 10 or 11, wherein the two zones are separated by a diaphragm (5).
13. Method according to one of Claims 10 through 12, wherein the solvent filling the chamber is liquid N_2H_4 or NH_3 or any other solvent that is chemically compatible with the stability of III-V nitrides.
14. Method according to one of Claims 10 through 13, wherein the seeds are composed of segments of single crystal or polycrystalline material.
15. Method according to Claim 14, wherein the seed material has lattice parameters that are compatible with those of the bulk single crystal network to be obtained.
16. Method according to Claim 14, wherein the segments of the seeds are oriented so as to ensure heteroepitaxy.
17. Method according to one of Claims 10 through 16, wherein crystallogenesis is performed in the presence of at least one precursor.
18. Method according to Claim 17, wherein the precursor is selected so as to produce anions such as N^{3-} .
19. Method according to Claim 17 or 18, wherein the precursor is an alkali or earth-alkali nitride.
20. Method according to Claim 17, wherein the precursor is Li_3N .
21. Bulk single crystal comprising nitrides of Group III elements, obtained by the method in any of Claims 1 through 20.
22. Single crystal according to Claim 21, wherein the single crystal is gallium nitride.
23. Single crystal according to Claim 21, wherein the single crystal is gallium alloy nitride.

24. Single crystal according to Claim 23, wherein the single crystal is one of the following nitrides: GaInN, AlGaN, GaAlInN, or any other nitride alloy implementing at least one of the Group III elements.
25. Microcrystallites of gallium nitride or of one of its alloys, approximately 1 μm in dimension, realized according to the first stage of the method described in any of Claims 1 through 9.

